

**THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN**

**IPC TECHNICAL PAPER SERIES  
NUMBER 231**

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**MARCH, 1987**

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Portions of this work were used by RCK as partial fulfillment of the requirements for the Master of Science degree at The Institute of Paper Chemistry. This paper will be presented at the TAPPI Delignification Conference in San Diego, CA on June 7-12, 1987

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## CATALYSIS IN PEROXIDE DELIGNIFICATION

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### ABSTRACT

Several aspects of catalysis in hydrogen peroxide delignification of kraft pulp have been experimentally investigated. These include catalysis of peroxide decomposition and delignification and inhibition of carbohydrate degradation. The behavior of unbleached southern pine kraft pulp in alkaline hydrogen peroxide parallels that of lignin model compounds, which are degraded at a rate that increases as the rate of peroxide decomposition is increased. Unlike the models, however, the pulp reacts, albeit more slowly, with peroxide that is not decomposing at an appreciable rate. Adding manganese ion to the pulp before delignification with 2%  $H_2O_2$  at 10% consistency sharply decreases the residual peroxide concentration and decreases the amount of lignin removed, but only slightly. Apparently, the effects of active oxygen loss balance or outweigh the beneficial effects of increased concentrations of reactive decomposition intermediates. Manganese addition improves the selectivity of delignification by inhibiting carbohydrate degradation. The effects of iron, copper and cobalt on delignification and carbohydrate degradation were also investigated and compared with those of manganese.

### INTRODUCTION

Hydrogen peroxide has considerable potential for commercial use in delignifying unbleached kraft pulps prior to final bleaching in either non-chlorine or conventional sequences (1). In its present state, the technology cannot compete with that already developed for using oxygen for the same purpose. The main reason is the high cost of hydrogen peroxide relative to that of oxygen, a circumstance that outweighs its advantages of simplicity of storage and application. On the other hand, peroxide has not been as extensively studied as oxygen, and some aspects of its behavior suggest that further study may point the way to improvements in efficiency that will offset its higher cost. Not the least of these is the sensitivity of the course of its reactions to the presence of trace amounts of transition metal ions and their complexes. The purpose of this paper is to further explore the role of catalysts in peroxide delignification.

Hydrogen peroxide's unparalleled ability to brighten mechanical and other high yield pulps has occasioned numerous studies, both fundamental and applied, of its effectiveness in this application. From these it has been learned that brightening occurs as a result of oxidation of lignin chromophores by the perhydroxyl anion, and that

chromophore elimination is not accompanied by appreciable yield loss. Research on the peroxide oxidation of lignin model compounds (2,3) has accordingly shown that neither hydrogen peroxide nor its anion is capable of oxidizing structural moieties representing the basic lignin skeleton. On the other hand, these same structures are extensively oxidized in peroxide solutions undergoing spontaneous decomposition, presumably as a result of attack by intermediates such as the hydroxyl radical and the superoxide anion radical. Such model studies will provide insight into the mechanism of peroxide delignification of pulps if parallel behavior can be established. An additional purpose of the present study was to determine this degree of similarity.

### CATALYSIS AND INHIBITION

To the extent that hydrogen peroxide's behavior toward the lignin in pulp resembles its reactions with model compounds, the link between delignification and peroxide decomposition presents a dilemma. Decomposition is necessary for delignification and is therefore beneficial. On the other hand, it is potentially detrimental because it results in conversion of the peroxide to oxygen, which is much less reactive and which would probably be lost. It is apparent that decomposition must be controlled at some desirable level. It may, for instance, be necessary to moderate the effect of decomposition catalysts by adding an inhibitor. Inhibitors may also be needed to protect the cellulose from attack by reactive peroxide-derived species.

The optimum level of peroxide decomposition can only be determined by simultaneously monitoring the rates of both the delignification and peroxide decomposition reactions. In the present study, this was accomplished by carrying out reactions in a closed vessel equipped with a gas collection and measurement system, as described elsewhere (3,4). This allowed continuous determination of the amount of oxygen evolved, making it possible to continuously monitor the decomposition reaction. Iodometric determination of residual peroxide at the end of a reaction gave the total amount of peroxide reacted and, by difference, the amount consumed by the pulp.

### Decomposition of Hydrogen Peroxide

A prerequisite to determining the effect of decomposition rate on delignification rate is the achievement of controlled decomposition rates, both in the presence of pulp and in its absence. This is made difficult, especially at the elevated temperature and pH necessary for delignification, by the extreme sensitivity of hydrogen peroxide to trace amounts of transition metals under these conditions. Even with the use of ultrapure reagents and extremely rigorous apparatus cleaning procedures, it is not possible to eliminate catalyzed decomposition (3). In this study, reproducibly low rates were obtained by supplementing these measures with the addition of 10 ppm magnesium ion as magnesium sulfate.

Southern pine kraft pulp (kappa number 37.3, permanganate number 24.1) was reacted with 73 mM

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hydrogen peroxide at pH 10.5 and 75°C, the pulp consistency being 0.54%. Duplicate controls with no pulp present were also run. Additional reactions were carried out at consistencies of 0.54, 0.77 and 1.08% after pretreating the pulp with diethylenetriaminepentaacetic acid (DTPA) and sodium bisulfite, as described by Gellerstedt (6). Table 1 contains metal ion contents of the untreated and pretreated pulps, and also of a sample that had been simply washed with  $\text{SO}_2$  solution.

Table 1. Metal analyses of pulps<sup>a</sup>

Sample	Metal Ion Content, ppm		
	Fe	Cu	Mn
Untreated	40	34	52
	37	29	58
$\text{SO}_2$ washed	49	8.5	4.0
DTPA- $\text{NaHSO}_3$ pretreated	28	5.0	3.3

<sup>a</sup>By atomic absorption spectrometry.

As shown in Figure 1, addition of untreated pulp to the alkaline peroxide solution caused a sharp increase in the rate of oxygen evolution. Pretreated pulp, on the other hand, caused no increase in decomposition rate, even when its consistency was doubled. This shows that the metals remaining in the pulp after pretreatment are not active as decomposition catalysts, perhaps because they are so tightly bound to the pulp. Interestingly, it also shows that the surfaces of the fibers themselves do not catalyze peroxide decomposition.

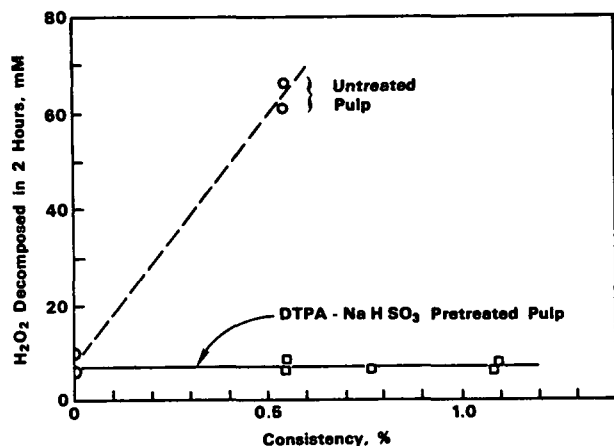


Fig 1. Effect of pulp consistency on peroxide decomposition rate as measured by oxygen evolution. Conditions: 75°C, pH 10.5, initial hydrogen peroxide concentration 73 mM, 10 ppm  $\text{Mg}^{++}$ .

The inactivity of the pretreated pulp made it a suitable substrate for determining the effect of added metal ions on the rates of decomposition and delignification. Figure 2 shows the effect of adding manganese to the pulp by allowing it to equilibrate with a solution of  $\text{MnSO}_4$  before thickening to 20% consistency. When added to alkaline hydrogen peroxide, the manganese enriched pulp catalyzed decomposition to a degree that depended on its Mn content.

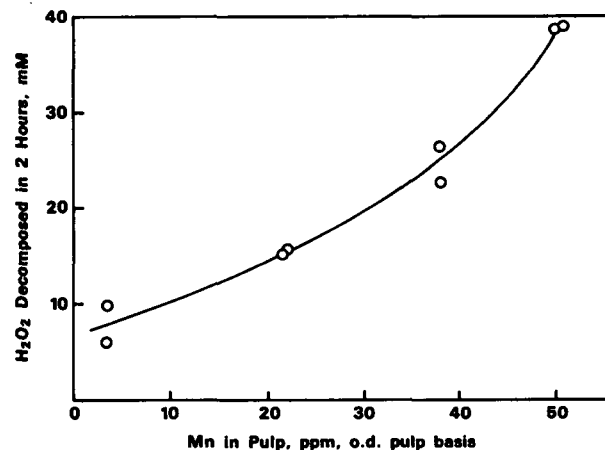


Fig. 2. Effect of pulp Mn content on peroxide decomposition rate. Pulp consistency 0.54%; other conditions as in Fig. 1.

### Delignification

Unpublished studies of the kinetics of hydrogen peroxide delignification (5,7) have given strong indications of a dependence of the extent of delignification by hydrogen peroxide on the rate of its decomposition. Figure 3 contains data from these studies and compares the delignification rates of the same pulp with and without added silicate but under otherwise similar conditions. In the absence of silicate, decomposition was rapid and continual additions of hydrogen peroxide were necessary to keep its concentration constant. Silicate addition so inactivated the traces of metal ions present that no decrease in peroxide concentration could be detected. Delignification was significantly faster in the rapidly decomposing solution, suggesting a parallel between the behavior of the lignin in wood and the model compounds already referred to.

**Effect of Consistency.** Table 2 contains the results of determinations of the degree of delignification for those experiments in Figure 1 that were run with pretreated pulp as the substrate. There was no effect of consistency on extent of delignification. This was true in spite of the fact that, because the concentration of peroxide in the liquid phase was the same for all experiments, the peroxide charge based on pulp was halved in going from the lowest to the highest consistency. This suggests that delignification is effected by short-lived decomposition intermediates that react with

the fiber only if they are formed in close proximity to it. Increasing the concentration of fibers utilizes a greater fraction of the amount of any given active species present, before it is converted to an inactive form. Below some critical consistency, any given fiber would then find itself in the same environment, regardless of how many neighbors it had. It may be speculated, for example, that superoxide radical anions are converted to oxygen unless they are formed close enough to a lignin surface to first react with it. Similar speculations may be made about hydroxyl radicals, oxide radical ions, ozonide ions and singlet oxygen.

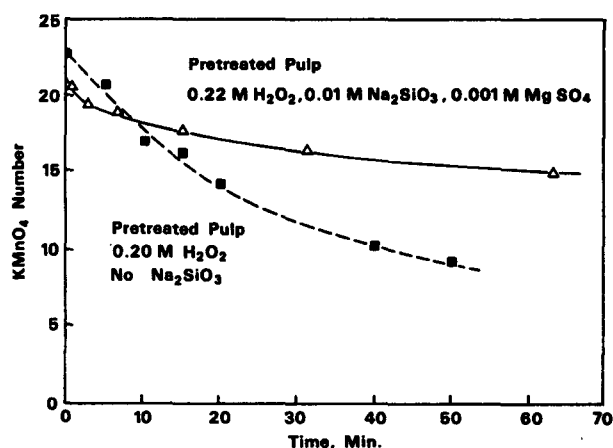


Fig. 3. Effect of peroxide stabilization on rate of delignification (5,7). Conditions: 73°C, pH 10.

Table 2. Effect of consistency on delignification in 73 mM H<sub>2</sub>O<sub>2</sub>

Consistency, %	Permanganate No. After Delignification
0.54	14.7
0.54	15.3
0.77	15.0
1.08	15.0
1.08	14.3

**Effect of Decomposition Rate.** By varying the extent of removal of "native" metal ions and varying the amount of metal ions added back to a previously purified pulp, it is possible to obtain a series of pulp samples that differ with respect to their ability to catalyze peroxide decomposition. Figure 4 shows the results of such a series of experiments. The correlation between the rates of delignification and decomposition is unmistakable, and confirms the behavior predicted by earlier

model compound studies. It should, however, be noted that the efficiency of peroxide use is higher at lower decomposition rates, because of the higher residual peroxide concentrations.

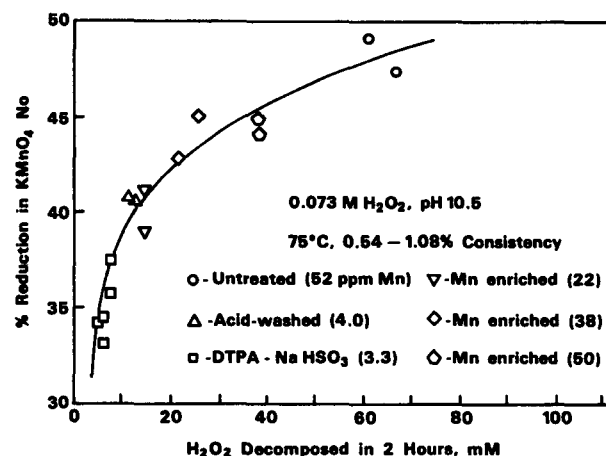


Fig. 4. Effect of peroxide decomposition rate on delignification rate.

**Stoichiometry.** Subtracting the amount of peroxide corresponding to the volume of evolved oxygen from the total decrease in the amount of peroxide present gave an estimate of the amount consumed by the pulp. Because it was obtained as a relatively small difference between two experimentally determined quantities, it was quite variable and significant trends were difficult to discern. Nevertheless, it is interesting that the average of all 15 observations, 4.5 moles H<sub>2</sub>O<sub>2</sub>/C9 unit, compares favorably with the values of 3.8-4.2 determined in a previous model compound study (4). This high value represents an opportunity for improving the efficiency of the process, since it seems unlikely that more than 1 or 2 moles of peroxide are necessary to solubilize a C9 unit. The remaining peroxide is presumably consumed in oxidizing soluble fragments, as indicated by model compound studies.

**Simulated Commercial Bleaching.** The results described above were obtained under conditions of low consistency and high peroxide availability to simplify the experiments and their interpretation. The absence of a consistency effect in the 0.5-1.0% range suggests that further increasing the consistency while maintaining the bulk liquor peroxide concentration approximately constant should have little effect on the degree of delignification obtained. The literature provides support for this inasmuch as similar degrees of delignification have been obtained at 10% consistency with a peroxide charge of 1.5% based on the dry pulp weight, which results in initial peroxide concentrations similar to those used in the experiments described above (8). Our experiments also show that increasing the rate of peroxide decomposition can increase delignification. Taken together, these observations imply the possibility that increased rates of decomposition may be beneficial, even at high

consistency and low peroxide charge. In view of this, it is of interest to examine the effect of adding decomposition catalysts such as manganese to peroxide bleaches carried out under such commercially feasible conditions.

Figure 5 shows the effect of adding manganese to pulp which had been pretreated with DTPA, HCl and  $\text{SO}_2$  to remove metal ions. A slight decrease in lignin removal was observed, instead of the hoped-for increase. As expected on the basis of the known catalytic effect of manganese on the rate of decomposition (Figure 2), residual peroxide, as % of the applied amount, decreased from 45 with no added Mn to 1.2 at 25 ppm Mn and 0 at 50 and 100 ppm. Although no improvement was observed, the fact that the degree of delignification remained nearly constant in the face of such a large potential loss of active oxygen attests to the existence of a catalytic effect of manganese on the rate of the delignification reaction. Apparently this beneficial effect was outweighed by the increase in the amount of peroxide converted to inactive oxygen.

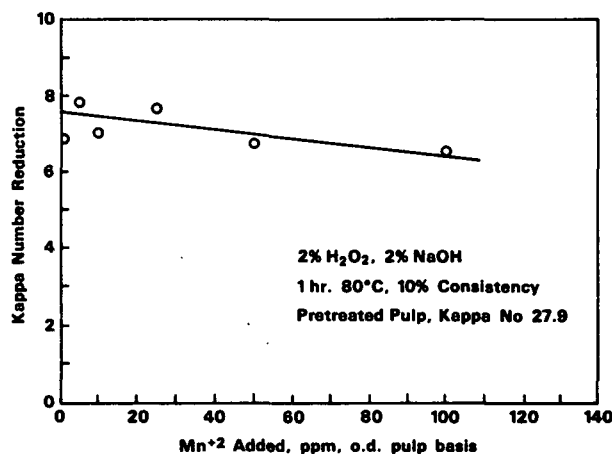


Fig. 5. Effect of manganese addition on degree of delignification.

A factor which may contribute to the failure of Mn addition to improve delignification is the existence of uncatalyzed peroxide delignification reactions. The experiments illustrated in Figure 3 provide evidence for the existence of these; addition of silicate virtually stopped decomposition, but delignification continued, albeit at a rate slower than in the presence of decomposing peroxide. Accelerated decomposition would decrease the extent to which uncatalyzed reactions occur by reducing the concentration of hydrogen peroxide.

Very small additions of manganese had a detrimental effect, which disappeared as the amount of Mn added was increased (Figure 6). This may indicate that the manganese ions themselves are in some way involved in the delignification reaction. Small additions efficiently catalyze peroxide decomposition, whereas larger amounts may be required for reaction with lignin. The formation of phenoxy

radicals, which is believed to be a prerequisite for delignification, is one candidate for direct involvement of metal ions (4).

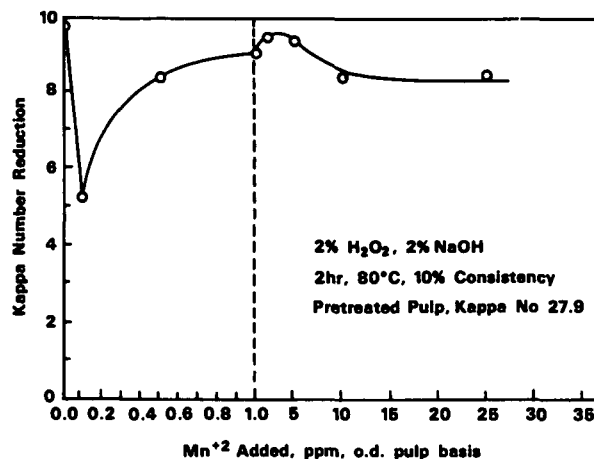


Fig. 6. Effect of low levels of manganese addition on degree of delignification. Note the discontinuity and change in the horizontal scale.

Addition of metal ions other than manganese was also of interest, in view of differences among them in their abilities to catalyze peroxide decomposition and generate phenoxy radicals, as well as possible unknown differences. Figure 7 compares the effects on delignification of Mn, Fe, Cu and Co at 2 levels of addition. The observed effects were generally similar to those of Mn, in that delignification was affected slightly or not at all, while residual peroxide was sharply decreased. An exception was iron, which, at the 10 ppm level, significantly decreased the extent of delignification. It may be significant that iron is known to be a less effective former of phenoxy radicals than either copper or manganese (9).

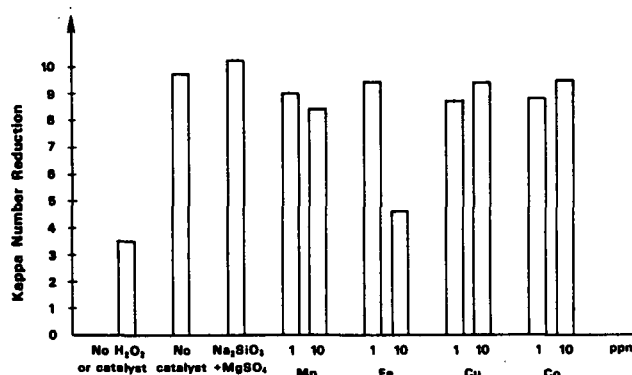


Fig. 7. Effect of addition of various metal ions on degree of delignification.

## Carbohydrate Degradation

Peroxide delignification of kraft pulp is usually accompanied by significant cellulose degradation, as manifested by a decrease in pulp viscosity. For example, delignification of pretreated unbleached southern pine pulp with 2%  $\text{H}_2\text{O}_2$  and 2%  $\text{NaOH}$  at  $80^\circ\text{C}$  caused the viscosity to fall from 23.4 to 18.2 mPa-s in 1 hour and to 14.5 in 2 hours. Addition of manganese retarded carbohydrate degradation, as shown in Figure 8. Because it retarded delignification only slightly, this resulted in a selectivity improvement, as illustrated in Figure 9.

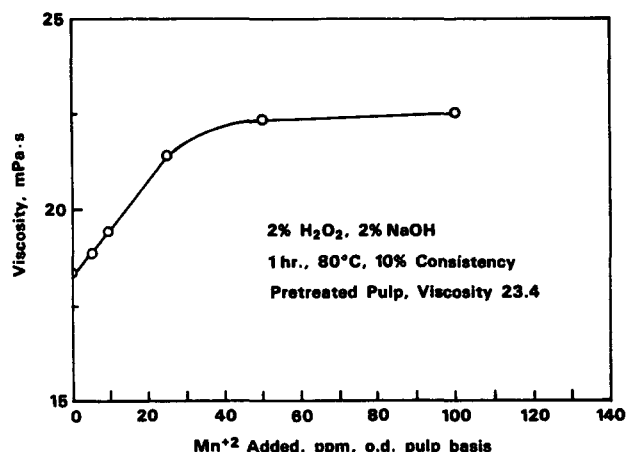


Fig. 8. Effect of manganese addition on pulp viscosity.

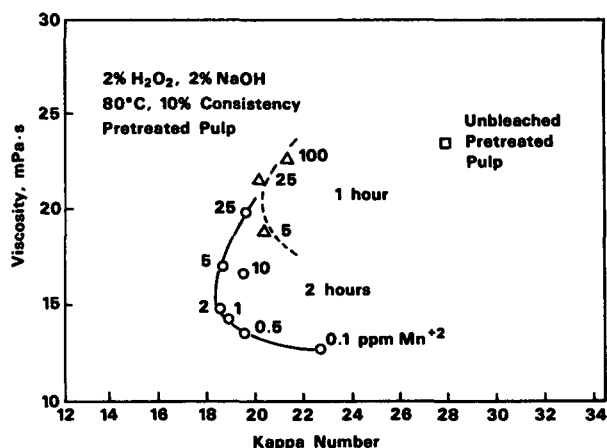


Fig. 9. Effect of manganese addition on selectivity at two retention times.

Manganese is known to have a similar protective effect during oxygen bleaching. Gilbert *et al.* (10) explained the effect in terms of adsorption of transition metal ions on the surface of precipitated hydrous manganese oxides. Such a mechanism may also be operative in the peroxide system. An

alternative possibility is that manganese improves selectivity by increasing the concentration of phenoxy radicals in lignin, making it more reactive and better able to compete with cellulose for reactive peroxide-derived species.

Other ions were also tested for their effects on viscosity retention, with the results shown in Figure 10. The protective effects of copper and cobalt were slight or nonexistent, but iron very effectively prevented carbohydrate degradation. The latter observation is, however, of little practical interest, since iron also interfered with delignification.

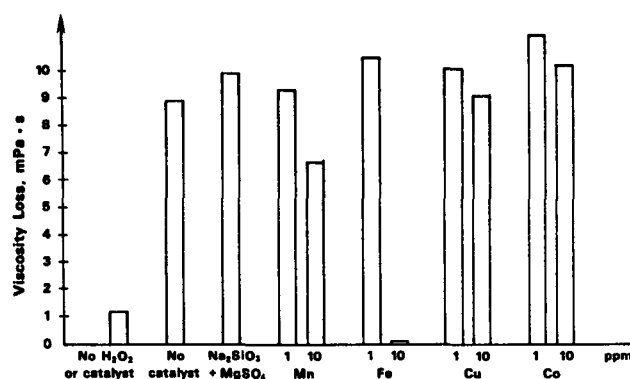


Fig. 10. Effects of addition of various metal ions on pulp viscosity.

## EXPERIMENTAL

### Materials

All pulps were prepared in the laboratory in an indirectly heated digester. Logs of southern pine, tentatively identified as loblolly pine were chipped and screened on site. Pulping runs were conducted at  $165\text{--}173^\circ\text{C}$  with liquor containing 16-18% effective alkali at 25% sulfidity. The pulps were screened on a laboratory flat screen with 0.009 inch slots.

All water used for pulp pretreatments, washing and bleaching was distilled in a Corning Mega-Pure still equipped with two high capacity deionizing resins.

Hydrogen peroxide was analytical reagent (AR) grade 30% solution from Atomergic Chemetal Co., Plainview, NY. Ultrapure sodium hydroxide was purchased as a 30% solution from Alfa Chemicals, Danvers, MA, and was used in the experiments during which decomposition rates were monitored. The polyethylene bottle was stored in a sealed jar over Ascarite. AR grade  $\text{NaOH}$  was used in the simulated commercial bleaches. The following were purchased as AR grade reagents and used without further purification:  $\text{DTPA}$ ,  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{NaHSO}_3$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ .

## Pretreatments

**SO<sub>2</sub> Wash.** SO<sub>2</sub> treatment prior to simultaneous determination of decomposition and delignification rates was carried out as follows: 100 g pulp was suspended in 5 L of a saturated solution of SO<sub>2</sub> in a polyethylene vessel for 10 minutes. It was then dewatered in a polyethylene Buchner funnel and washed with distilled and deionized water.

**DTPA-NaHSO<sub>3</sub> pretreatment** was carried out according to Gellerstedt (6).

**DTPA-HCl-SO<sub>2</sub> Pretreatment.** Pulp (kappa No. 31.7, viscosity 26.4 mPa·s, 41 ppm Mn, 30 ppm Fe, 5 ppm Cu, 331 ppm Mg, 72 ppm N) was disintegrated in a British disintegrator at 2% consistency for 20 min. DTPA was added in an amount equivalent to 0.4% of the dry pulp weight to give a pH of 2.6. After 24 hours with occasional stirring the pulp was dewatered, washed with distilled water and extracted in a Soxhlet extractor for 24 hours with distilled and deionized water. After replacing the water with fresh distilled and deionized water the extraction was repeated.

The extracted pulp was suspended at 2.5% consistency in 1N HCl, stirred for 5 minutes, and allowed to stand for 1 hour. It was then dewatered, washed to pH 4.5, dewatered, and suspended at 2% consistency in SO<sub>2</sub> solution at pH 3. Finally the pulp was washed to pH 5 and again dewatered. The resulting pulp had kappa No. 27.9, viscosity 23.4, < 2 ppm Mn, 6 ppm Fe, 0.1 ppm Cu, and 199 ppm N.

**Mn Enrichment.** To 30 g DTPA - NaHSO<sub>3</sub> pretreated pulp was added 2.0, 4.0, or 6.5 mL of 0.895 g/L MnSO<sub>4</sub> and the slurry, after mixing, was stored for four days at 4°C before dewatering to 20% consistency.

## Peroxide Delignification

Bleaches were conducted either in a Teflon lined, magnetically stirred reactor equipped with a gas collection and measurement system, or in plastic bags. In the former case, pH and volume of oxygen evolved were continuously monitored. All reactor surfaces were rigorously cleaned before each run by scouring with detergent, followed by successive rinses with distilled and deionized water, acetone, 35% nitric acid, and copious amounts of distilled and deionized water. All reactions in this reactor were conducted at pH 10.5 and 75°C in the presence of 10 ppm of added magnesium ion. The volume of oxygen evolved was measured in a water jacketed gas buret. It was adjusted to standard conditions and corrected for dissolved oxygen. At the end of the reaction, the reactor contents were filtered and the filtrate was quenched in an ice bath before being iodometrically titrated for residual peroxide. The pulp was washed with 1% NaHSO<sub>3</sub>, followed by copious amounts of distilled water, before being analyzed.

Bleaches in plastic bags were conducted as follows: 25 o.d. g pulp was placed in the bag and diluted to 10% consistency by successive additions of dilution water, Mn solution, H<sub>2</sub>O<sub>2</sub> and NaOH. The

bag was then closed, mixed by hand kneading and placed in a thermostatted water bath for the required time. After bleaching the pulp was filtered and washed, and the filtrate was immediately analyzed for pH and residual peroxide.

## Test Methods

TAPPI test methods were used for kappa number (T236 OS-76) and viscosity (T230 OS-76). Permanganate numbers were determined by a scaled down version of TAPPI Useful Method 251: 0.1 g pulp was dispersed in 112 mL water; 4 mL 4N H<sub>2</sub>SO<sub>4</sub> and 4 mL 0.1N KMnO<sub>4</sub> were added and the suspension was held at 25°C for 5 min. with constant stirring before adding KI and titrating with 0.01N thiosulfate.

Metal ion contents were determined either by atomic absorption spectrometry or plasma emission spectrometry.

## CONCLUSIONS

1. Unbleached southern pine kraft pulp (USPKP) that has been pretreated to remove metal ions does not catalyze alkaline hydrogen peroxide (AHP) decomposition in the presence of 10 ppm magnesium ion. By implication, neither the fiber surfaces nor the tightly bound residual transition metal ions are catalytic.

2. At constant peroxide concentration, USPKP is delignified significantly more rapidly by decomposing AHP than by AHP in which decomposition has been virtually arrested by addition of sodium silicate. Delignification is, however, not stopped by stopping the decomposition, showing that not all of the reactions responsible for delignification are due to decomposition intermediates.

3. Pretreated USPKP added to slowly decomposing AHP at an initial hydrogen peroxide concentration of 73 mM is delignified at a rate which is independent of the amount of pulp present, over the consistency range from 0.54 to 1.08%. This implies that the species responsible for delignification do not survive long enough to travel appreciable distances from their points of origin. Increasing the fiber population density utilizes more of these species.

4. Delignification of USPKP in AHP initially 73 mM in H<sub>2</sub>O<sub>2</sub> proceeds at a rate that increases with increasing H<sub>2</sub>O<sub>2</sub> decomposition rate when the latter is manipulated by removing metal ions from the pulp or adding manganese to the pulp.

5. Adding manganese to USPKP before delignification with 2% H<sub>2</sub>O<sub>2</sub> and 2% NaOH at 10% consistency slightly decreases the extent of lignin removal. Apparently, the effects of active oxygen loss balance or outweigh the beneficial effects of increased concentrations of reactive decomposition intermediates.

6. The effects of additions of copper and cobalt on delignification are similar to those of manganese. Residual peroxide concentrations are sharply decreased, while lignin removal is unchanged or slightly decreased.



7. Manganese is effective in retarding carbohydrate degradation during AHP delignification of USPKP and therefore improves selectivity. Cobalt and copper do not have similar effects. Iron stops carbohydrate degradation but also interferes strongly with delignification.

#### ACKNOWLEDGMENT

Portions of this work were used by (R.C.K.) as partial fulfillment of the requirements for the Master of Science degree at The Institute of Paper Chemistry.

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